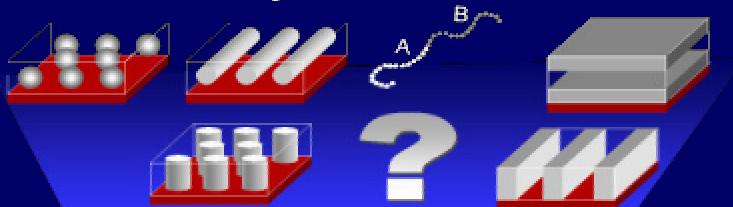


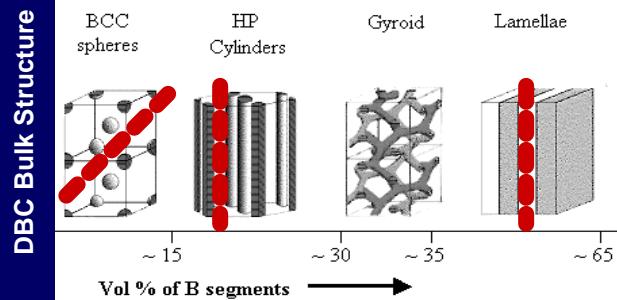
Diblock Copolymer Thin Films and the Double Gyroid Motif – A Gradient Study

Does the Double Gyroid Motif Persist in Thin Films?



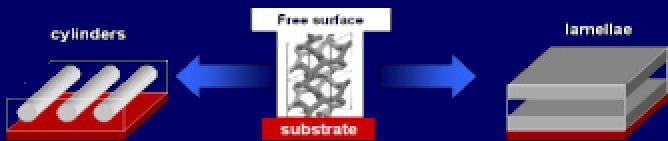
Why it Matters:

- The Double Gyroid (DG) motif is continuous in both phases.
 - Percolating pores: membrane applications.
- The DG has cubic symmetry.
 - Photonics Applications
- DG film behavior is unknown.
 - The missing link in DBC film studies



DG films present unique circumstances:

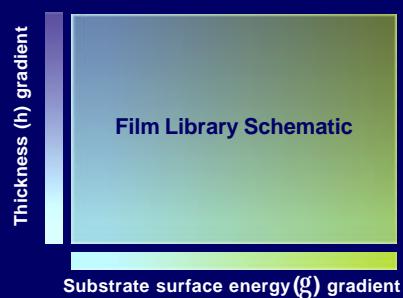
- DG structure cannot support complete wetting of the substrate or film surface with A or B without disrupting the motif. All other forms can exhibit single block wetting while maintaining the domain shape (red dashed lines).
 - Accordingly, DG species may exhibit "motif shifts" to accommodate substrate/surface wetting conditions.



Experiment Design:

A Crossed-gradient combinatorial library that maps the thin film behavior of DG-exhibiting DBC Specimens

Gradients in the variables that govern DBC film structure



- Library covers every combination of h and g within the gradients' scope.
- Typical size: 10cm x 10cm
- h: 10 to 70nm
- g: 25 to 75 mJ/m²
- film surface energy is **not** controlled

Experiment System:

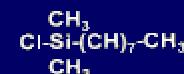
Diblock Copolymer

- Polyisoprene-b-Polystyrene
- Mn=23.8K, 37wt% PS
- DG in bulk (TEM, SAXS)
- Period (L) » 27 nm

Substrate

- Single crystal Si wafer
- Piranha Sol'n Cleaned
- UV-ozone treated

Self-Assembled Monolayer (SAM)

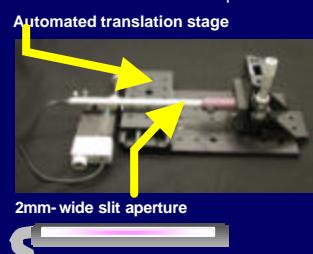


- Basis of g-gradient
- n-octyldimethylchlorosilane (OCS)
- Deposited on Si from vapor. Rinse in Toluene.
- 120 °C/Vacuum, 2 hrs.

Library Fabrication: Gradient Techniques Developed at the NIST Combinatorial Methods Center

Substrate g-Gradient

UV-Ozone Gradient Exposure Device



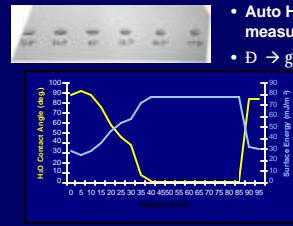
- 192nm UV wand source
- Generates O₃ and O
- SAM-treated substrate is mounted on stage, under slit aperture
- Stage acceleration creates exposure gradient

A gradient in SAM Chemistry



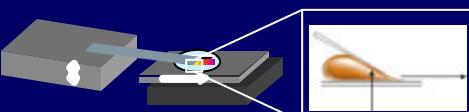
- O₃ and O impart low-g OCS SAM with hi-g species.
- Density of -OH and -COOH groups depends upon exposure time^{*}.

γ-gradient Characterization



Film thickness (h) Gradient

NIST Gradient Flow Coater



- Dilute (~1wt%) polymer sol'n injected between flat blade and substrate mounted on automated translation stage
- Stage acceleration deposits film with h-gradient[†]

h-gradient Characterization

- UV-vis Spot Interferometer (0.5mm footprint)
- Computer controlled X and Y translation stages enable automated mesh of thickness measurements.

[†]J.C. Meredith et al, Macromolecules, Vol. 33, No. 26, 2000

M.J. Fasolka¹, A. Karim¹, E.J. Amis¹, A.M. Urbas² and E.L. Thomas²

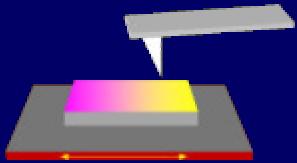
¹Polymers Division • NIST • Gaithersburg, MD / ²Dept. Mat. Sci. and Eng. • MIT • Cambridge, MA

Diblock Copolymer Thin Films and the Double Gyroid Motif – A Gradient Study

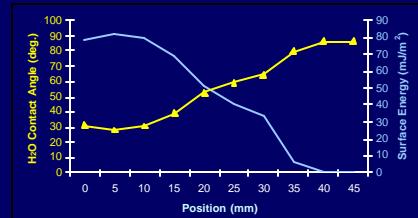
Preliminary Results: Constant Thickness (Spin Coated, $h \gg 46$ nm) Film on g-Gradient

Surface Morphology:

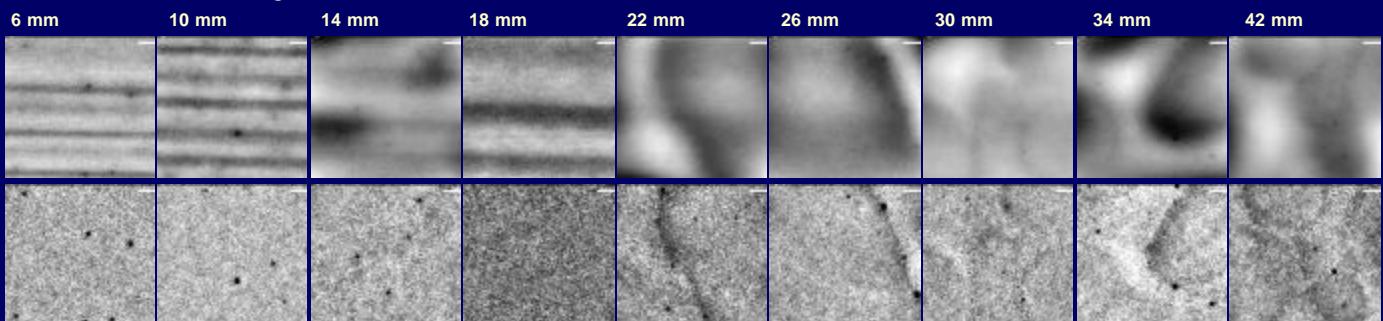
- Programmable AFM
- Height and Phase Imaging
 - PS-PI gives good contrast
- 2 mm image scans
- Scale bar: 250nm



Surface Energy Gradient



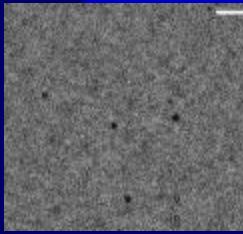
Micrograph position on g-gradient:



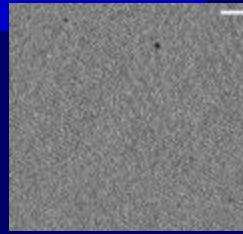
Height Data, scale: 30nm

Phase Data, scale: 30°

Some further exploration

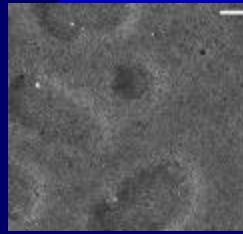


Perforated lamella?

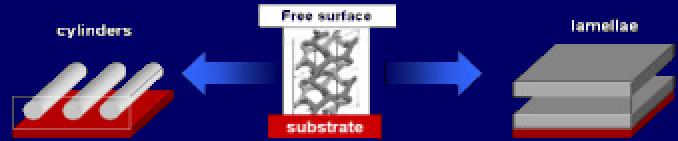


Spheres or ^ Cylinders

Motif Shifts



|| Cylinders or ^ lamella, some || Lamella?



Conclusions so far:

- No Double Gyroid was observed
- Shifts in motif to lamella, cylinders and possibly even spheres was observed

Future Directions:

- Incorporation of thickness gradient for true combinatorial experiment (and more data)
- Use of selective PI etching (plasma) to better illuminate structure. Library will be imaged both before and after etching.
- Wider range of micrograph scales.



NIST
Combinatorial
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